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EFFECT OF REDOX CATALYSTS ON OXIDATIVE DEGRADATION OF COTTON LIGNIN

V. E. Madzhidova, Kh. A. Abduazimov, and Kh. S. Akhmedkhodzhaeva

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The effects of anthraquinone and demethylated lignin on the oxidation of cotton lignin are compared. Results of the estrogen activity of certain aromatic acids are presented.

Key words: cotton lignin, oxidation, redox catalysts.

Redox catalysts, anthraquinone (AQ) and demethylated lignin (DML), the activity of which is based on the conversion of lignin into low-molecular-weight phenolic compounds, were used by us during nitrobenzene oxidation of lignin dust from mature cotton stalks. The oxidation of lignin in alkaline medium includes hydrolysis, during which β-O-4-alkyl—aryl ether bonds in lignin macromolecules are broken [1]. Then, low-molecular-weight hydrolysis products are oxidized to aldehydes, ketones, and acids.

Demethylated lignin, like AQ, catalyzes delignification of wood, is more available, and is practically as effective as AQ as a polydisperse product containing condensed quinones. In the first reaction stage, AQ oxidizes terminal groups of cellulose and hemicellulose chains to stable aldone-acid groups and is itself reduced to anthrohydroquinone. Then it acts as a reductant and accelerates the cleavage of lignin bonds to carbohydrates and ether bonds between structural elements of lignin macromolecules [1].

During oxidation of natural lignin, cotton stalks, by nitrobenzene, 0.1% AQ and 1.0% DML of the dry mass are added. The yields of natural lignin oxidation products by AQ and DML in percent from lignin obtained by the Komarov method are given below:

Cotton stalks	Aldehyde fraction	Acid fraction	Total yield
Control (without catalyst)	8.86	8.53	17.39
0.1% AQ	8.80	14.32	23.12
1.0% DML	10.38	11.26	21.64

Experiments demonstrated that the yield of total oxidation products increases with AQ to 23% and with DML to 20% compared to reactions without catalysts. Oxidation by nitrobenzene of DML itself forms low-molecular-weight phenols (10.0%). If 1.0% DML is used as catalyst, the total oxidation products from DML increase by 0.41% from lignin by Komarov [2].

GLC identified in the total oxidation products aldehydes, ketones, and acids, the composition of which is given below (% from lignin by Komarov):

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 340-341, July-August, 2000. Original article submitted May 1, 2000.

Substance	AQ	DML	Without catalyst
Hydroxybenzoic acid	1.03	1.66	0.65
p-Coumaric acid	1.06	1.01	0.15
p-Hydroxybenzaldehyde	0.68	0.15	0.26
p-Hydroxyacetophenone	0.12	0.32	0.10
Vanillic acid	4.65	3.81	4.15
Guaiacol	2.32	3.58	2.28
Vanillin	4.64	4.13	4.10
Acetoguaiacol	-	0.09	-
Syringic acid	2.11	1.32	2.3
Syringic aldehyde	2.64	3.09	3.21

The content of compounds with the *p*-coumaric structure increases in the products from oxidation of cotton lignin in the presence of catalysts whereas that of those with the syringic acid structure decreases. The methoxyls of the syringic units of cotton lignin are probably partially cleaved in the presence of AQ and DML.

Thus, cotton stalks can provide a source of aromatic aldehydes, ketones, and acids. It should be noted that the content of vanillin, which is necessary for the food industry, is less than 23 and 2.13% of the starting material in the total oxidation products.

Several compounds that were obtained via oxidation and decomposition with sodium in liquid ammonia [3] and are derivatives of phenol and hydroxy- and methoxyphenylpropane [4] were investigated for estrogen activity. These compounds include *p*-hydroxybenzoic, gallic, anisic, vanillic, syringic, veratric, and ferulic acids and vanillic alcohol.

It was found that the estrogen effect was noticeable (90%) in compounds with a benzene containing a hydroxyl in para-position to a carboxylic group (*p*-hydroxybenzoic acid). The effect increases slightly (100%) if additional OH groups are placed on C-3 and C-5 (gallic acid). Replacing one (anisic and vanillic acids) or two (syringic acid) OH groups with methoxyls decreases the activity (veratric acid). Vanillic alcohol, which contains $–CH_2OH$ on C-1 and $–OCH_3$ and OH on C-3 and C-4, respectively, exhibits no estrogen activity. On the other hand, the phenylpropane structure of ferulic acid was more active. The estrogen activity of the studied compounds was estimated from the ability of neutered rats to reach estrus [7, 8].

EXPERIMENTAL

Oxidation of natural lignin, cotton stalks, by nitrobenzene was performed by the literature method [5]. Anthraquinone was added during the oxidation step at 0.1% of the mass of cotton stalks that had been ground and extracted with alcohol—benzene (1:2) and hot water. DML was added at 1.0% of the mass of cotton stalks. Chromatography was carried out on a Chrom-4 chromatograph with a flame-ionization detector. The total acids were analyzed as the methyl esters on a stainless-steel column (120 × 0.3 cm) packed with 4% PEGA on Chromaton-NAW-DMCS (0.165-0.200); carrier-gas (He) flow rate 50 ml/min; temperature 180°C.

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